

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2001-224969

(43)Date of publication of application : 21.08.2001

(51)Int.Cl.

B01J 37/03
B01J 23/40
H01M 4/88
H01M 4/90
// H01M 8/10

(21)Application number : 2000-039592

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(22)Date of filing : 17.02.2000

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(54) METHOD FOR PREPARING ALLOY CATALYST AND METHOD FOR MANUFACTURING SOLID HIGH-POLYMER TYPE FUEL BATTERY

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a method for preparing an alloy catalyst containing active metals which have a high alloying degree and are more pulverized.

SOLUTION: This method includes a state for preparing an alloy colloid solution by adding ≥ 2 kinds of metal salts to an aqueous solution in which a reducing agent consisting of an organic acid is dissolved at the same period in the state of dissolving the metal salts in water and a stage for depositing the alloy colloid particles in the solution on a carrier.

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CLAIMS

[Claim(s)]

[Claim 1]A preparing method of an alloy catalyst characterized by comprising the following.
A process of preparing an alloy colloidal solution by adding at the period in the state where water was made to dissolve two or more kinds of metal salt in solution in which a reducing agent which consists of organic acid is dissolved.

A process which makes a carrier support an alloy colloidal particle in said solution.

[Claim 2]A manufacturing method of a polymer electrolyte fuel cell provided with an anode pole and a cathode pole containing a catalyst and a polymer electrolyte characterized by comprising the following.

A process of preparing Pt content alloy colloidal solution by adding a catalyst of at least one electrode among said anode pole and said cathode pole at the period in the state where water was made to dissolve two or more kinds of metal salt (platinum salts are included) in solution in which a reducing agent which consists of organic acid is dissolved.

A process which makes carrier powder support Pt content alloy colloidal particle in said solution.

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]This inventions are a preparing method of an alloy catalyst, and a thing especially concerning the preparing method of the electrode catalyst for polymer electrolyte fuel cells, and the manufacturing method of a polymer electrolyte fuel cell.

[0002]

[Description of the Prior Art]With the catalyst which uses a single metal as an active metal, an alloy catalyst shows the unique catalytic activity which is not acquired, and is applied to the chemical process or various catalysts for flue gas treatment of petrochemistry and oil refining. These days, it is being used for the electrode catalyst for polymer electrolyte fuel cells.

[0003]An alloy catalyst is prepared by the method of fusing and alloying the metal of two or more ingredients at an elevated temperature (elevated-temperature reduction scorification), or making metal dissolving with physical means, such as sputtering. However, according to these methods, since melting of the metal is carried out and it is alloyed, the particle diameter of alloy particles becomes large, the specific surface area of alloy particles increases, and there is a problem that high catalytic activity is not acquired. The alloy electrode catalyst for fuel cells is made into an example, and such a problem is explained concretely.

[0004]Since the polymer electrolyte fuel cell can take out compact and high current density, it attracts attention as a power supply for an electromobile or spacecrafts. The thing which made the active metal which becomes a carrier which consists of carbon from Pt as such an anode electrode catalyst for fuel cells support is used. However, since poisoning of the catalyst which contains Pt as this active metal is carried out by CO which is easy to mix into the fuel gas containing hydrogen, it has the problem of causing the fall of battery capacity.

[0005]Since it is such, controlling poisoning by CO is performed by applying the alloy which consists of the 2nd ingredient, Pt, Ru, etc., as an active metal of an anode electrode catalyst. In order to control poisoning by CO, it is necessary to make high the alloying degree of platinum and the 2nd ingredient of addition. For this reason, the active metal which consists of a Pt content alloy is produced by the elevated-temperature reduction scorification mentioned above or sputtering process.

[0006]However, since the particle diameter of an alloy would become large if Pt content alloy is formed by elevated-temperature reduction scorification or sputtering process, high catalytic activity is not acquired and performance of the fuel cell was not able to be raised.

[0007]

[Problem(s) to be Solved by the Invention]The alloying degree of this invention is high and an object of this invention is to provide the preparing method of the alloy catalyst containing the active metal atomized more.

[0008]An object of this invention is to control that poisoning of the alloy catalyst which contains Pt content alloy as an active metal is carried out by CO, and to provide the manufacturing method of a highly efficient polymer electrolyte fuel cell.

[0009]

[Means for Solving the Problem]This invention is characterized by a preparing method of an alloy catalyst comprising the following.

A process of preparing an alloy colloidal solution by adding at the period in the state where water was made to dissolve two or more kinds of metal salt in solution in which a reducing agent which consists of organic acid is dissolved.

A process which makes a carrier support an alloy colloidal particle in said solution.

[0010]A manufacturing method of a polymer electrolyte fuel cell concerning this invention, In a manufacturing method of a polymer electrolyte fuel cell provided with an anode pole and a cathode pole containing a catalyst and a polymer electrolyte, Among said anode pole and said cathode pole, a catalyst of at least one electrode, A process of preparing Pt content alloy colloidal solution by adding at the period in the state where water was made to dissolve two or more kinds of metal salt (platinum salts are included) in solution in which a reducing agent which consists of organic acid is dissolved, It is produced by a method of providing a process which makes carrier powder supporting Pt content alloy colloidal particle in said solution.

[0011]

[Embodiment of the Invention]Hereafter, the preparing method of the alloy catalyst concerning this invention is explained.

[0012](Alloy colloid preparation process) An alloy colloidal solution is prepared by adding at the period in the state where water was made to dissolve two or more kinds of metal salt in the solution in which the reducing agent which consists of organic acid is dissolved.

[0013]. As the addition method of metal salt, add the mixed water solution in which metal salt beyond (a)2 kind is dissolved, for example. (b) Adding one or more kinds of mixed water solutions of (c) above (a) and one or more kinds of independent solution of the above (b) which prepare two or more kinds of solution in which one kind of metal salt is dissolved, and add these solution at the period at the period etc. is mentioned.

[0014]After the solution in which the reducing agent which consists of said organic acid is dissolved boils water and removes dissolved oxygen, for example, it is preferred to prepare by dissolving organic acid. It is because it is easy to generate an oxide, it becomes easy to condense an alloy colloidal particle with this oxide and the particle diameter of a colloidal

particle may become large, if dissolved oxygen is contained in said solution.

[0015]said organic acid -- alcohols (for example, methanol, ethanol, and isopropanol.) butanol and citrate (for example, sodium acid citrate and potassium citrate.) Ammonium citrate and ketone (for example, acetone, methyl ethyl ketone). It is preferred to consist of at least one kind of organic acid chosen from carboxylic acid (for example, acetic acid, formic acid, fumaric acid, malic acid, aspartic acid, amber acid) and ester species (for example, formic acid methyl).

[0016]The presentation in particular of the alloy colloid prepared is not limited, but is made into the thing according to the presentation of the catalyst made into the purpose. As for the presentation of alloy colloid, when producing the catalyst of the electrode for polymer electrolyte fuel cells, it is preferred to make it what consists of at least one kind of element chosen from Pt, Ru and Au, Pd, Rh, Ir, Co, Fe, nickel, Cu, and Sn.

[0017]As said metal salt, metal chloride, a metal nitrate, a metal complex, etc. can be mentioned, for example. If an example of metal chloride is given, there will be chloroplatinic acid and dinitrodiamine platinum salts will be mentioned as an example of a metal complex.

[0018]It is preferred to add at the period in the state where water was made to dissolve two or more kinds of metal salt in the solution in which the reducing agent which consists of organic acid is dissolved, and to hold these at 30-110 °C. Since alloy formation reaction velocity can be made moderate by having such composition, an alloy colloidal solution can be prepared with sufficient mass production nature. The more desirable range is 40-110 °C.

[0019](Support process to the carrier of alloy colloid) An alloy catalyst is acquired by making carrier powder support the alloy colloidal particle of the obtained alloy colloidal solution.

[0020]In support to carrier powder, it is a liquid-phase-adsorption method (after making an alloy colloidal particle stick to said carrier powder by adding and stirring carrier powder to the alloy colloidal solution of a room temperature), for example. the method of filtering, washing and drying -- it is -- the evaporating method (it is the method of heating adding and stirring carrier powder to an alloy colloidal solution, and dispersing a solvent) is employable.

[0021]In an alloy colloidal solution, the surplus ion generated by a reaction with a reducing agent may exist. In such a case, before performing support to carrier powder, it is preferred to remove the positive ion and negative ion which are surplus ion through an alloy colloidal solution on ion-exchange resin.

[0022]Said carrier powder in particular is not limited, but the thing according to the catalyst presentation made into the purpose is used. As said carrier powder, porous material (for example, alumina, silica), carbon system powder, etc. can be mentioned, for example. As said carbon system powder, black lead, carbon black, the activated carbon that has electric conductivity, etc. can be mentioned, for example. In particular, to the electrode catalyst for fuel cells, said activated carbon is preferred.

[0023]As for the holding amount of the active metal in the electrode catalyst for fuel cells, it is preferred to make it to not less than 10%. By making a holding amount not less than 10%, a fuel cell can be made more into high performance.

[0024]Subsequently, the manufacturing method of the polymer electrolyte fuel cell concerning

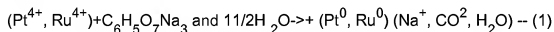
this invention is explained.

[0025]First, the alloy catalyst (let Pt content alloy be an active metal) prepared by the method mentioned above and a solid polymer electrolysis solution are added to solvents, such as ethanol, and the slurry for anode poles is prepared by stirring these. the alloy catalyst (let Pt content alloy be an active metal) prepared by the method mentioned above on the other hand - or the catalyst which uses Pt as an active metal, and a solid polymer electrolysis solution are added to solvents, such as ethanol, and the slurry for cathode poles is prepared by stirring these.

[0026]An electrode cell is produced by applying the slurry for anode poles to one field of a solid polymer electrolysis film, and applying the slurry for cathode poles to the field of another side. A charge collector like carbon paper is stuck on both sides of this electrode cell, and a single cell solid polymer fuel cell is obtained by laminating a separator to each charge collector. The presentation of said cathode terminal and said anode electrode can be made the same when using hydrogen for fuel.

[0027]By adding at the period in the state where water was made to dissolve two or more kinds of metal salt in the solution in which the reducing agent which consists of organic acid is dissolved according to the preparing method of the alloy catalyst which starts this invention as explained in full detail above, and preparing an alloy colloidal solution, Since each metal ion can be made to return simultaneously also when the oxidation reduction level differs mutually, the alloying degree of a colloidal particle can be made high. Since the reducing agent which consists of organic acid has weak reducing power compared with the hydrazine and thiosulfate salt which are used from the former, The reduction reaction (an example is shown in following the (1) type) of a metal ion can progress gently, the crystal growth by reduction can be controlled, and minuteness making of the alloy colloidal particle can be carried out (for example, particle diameter of 2-3 nm). The coefficient is omitted in (1) type.

[0028]



Since the alloying degree and specific surface area of an active metal can be raised by making carrier powder support the obtained alloy colloidal particle, the alloy catalyst by which activity has been improved and from which high activity will be acquired with a little active metals if it puts in another way can be provided. Since the activity of said catalyst can be improved by presenting a polymer electrolyte fuel cell with Pt content alloy catalyst acquired by the method of this invention and it can control that poisoning of said catalyst is carried out with carbon monoxide, the performance of a fuel cell can be improved.

[0029]In the conventional method which uses hydrazine and thiosulfate salt as a reducing agent, it is easy to condense the formed alloy colloid, and it necessary to add protective colloid, such as a surface-active agent. The alloy colloidal particle obtained by this invention can maintain the shape of a particle, even if protective colloid is not added.

[0030]By adding at the period in the state where water was made to dissolve two or more kinds of metal salt in the solution in which the reducing agent which consists of organic acid is

dissolved in the method concerning this invention, holding these at 30-110 **, and preparing an alloy colloidal solution, Mass production nature can be made high, controlling the crystal growth by reduction.

[0031]

[Example] Hereafter, the desirable example of this invention is described in detail.

[0032][Example 1]

Sodium-acid-citrate ($C_6H_5O_7Na_3$ and $11/2H_2O$) 10mmol is added to 1 l. of ion exchange water from which dissolved oxygen was enough removed by making it boil for <alloy colloidal solution preparation-> 1 hour, The solution uniform under 100 ** boil was prepared. The mixed water solution (Pt is [Ru] 1mmol in 1mmol) of chloroplatinic acid and ruthenium chloride was dropped at this solution, these were held at 100 **, and reduction processing was performed for 1 hour. After checking that a solution discolors black from red, it quenched to the room temperature. Shade and a positive ion were removed through the generated Pt-Ru alloy colloidal solution on ion-exchange resin, and it was considered as the alloy colloidal solution 1.

[0033] 0.5g of specific surface area adds to the <support to carrier of alloy colloid> 2 l. above-mentioned alloy colloidal solution 1, and carried out ultrasonic dispersion of the KETCHIEN carbon of $800\text{-m}^2/\text{g}$ to it, and the uniform slurry was obtained. Having kept the obtained solution at 90 ** and stirring it, by evaporating water, carbon was made to support alloy particles and the acquired carbon support Pt-Ru alloy catalyst was made into the catalyst 1.

[0034][Example 2] In preparation of an alloy colloidal solution, instead of sodium acid citrate, Except using ethanol, methanol, isopropanol, butanol, acetic acid, formic acid, acetone, methyl ethyl ketone, or formic acid methyl, as Example 1 mentioned above explained, the Pt-Ru alloy colloidal solutions 2-10 were prepared. Each alloy colloidal solutions 2-10 were made to support like Example 1 mentioned above to KETCHIEN carbon, and the acquired carbon support Pt-Ru alloy catalyst was made into the catalysts 2-10.

[0035] In preparation of an alloy colloidal solution, instead of ruthenium chloride, chloroauric acid, Except using a palladium chloride, a rhodium chloride, an iridium chloride, a cobalt chloride, ferric chloride, nickel chloride, a copper chloride, or tin chloride, The alloy colloidal solutions 11-19 which consist of Pt and an alpha element as Example 1 mentioned above explained were prepared (alpha element is Au, Pd, Rh, Ir, Co, Fe, nickel, Cu, or Sn). Each alloy colloidal solutions 11-19 were made to support like Example 1 mentioned above to KETCHIEN carbon, and the acquired carbon support Pt-alpha alloy catalyst was made into the catalysts 11-19.

[0036][Comparative example 1] After making carbon system powder support Pt and Ru with the impregnating method so that it may explain below, Pt and Ru were alloyed by high temperature heat treatment, and the carbon support Pt-Ru alloy catalyst was acquired.

[0037] That is, 0.4g of KETCHIEN carbon is sampled, and it was made to evaporate to dryness, chloroplatinic acid and a ruthenium chloride mixed water solution (Pt 2mmol, Ru 2mmol) being dropped at carbon, and kneading them. This was exposed to a 900 ** nitrogen atmosphere,

and after making a Pt-Ru alloy form by supplying hydrogen 1% for 1 hour, the carbon support Pt-Ru catalyst acquired by cooling to a room temperature was made into the comparison catalyst 1.

[0038][Comparative example 2] The mixed water solution (Pt is [Ru] 1mmol in 1mmol) of chloroplatinic acid and ruthenium chloride was previously added by making it boil for 1 hour to 1 l. of ion exchange water from which dissolved oxygen was removed enough. Subsequently, after having added sodium-acid-citrate 10mmol, holding these at 100 °C and performing reduction processing for 1 hour, it quenched to the room temperature, shade and a positive ion were removed through the generated Pt-Ru alloy colloidal solution on ion-exchange resin, and the alloy colloidal solution was prepared. This alloy colloidal solution was made to support like Example 1 mentioned above to KETCHIEN carbon, and the acquired carbon support Pt-Ru alloy catalyst was made into the comparison catalyst 2.

[0039][Comparative example 3] In preparation of an alloy colloidal solution, ruthenium chloride was not added, but except using only chloroplatinic acid, as Example 1 mentioned above explained, the platinum colloid solution was prepared. This platinum colloid solution was made to support like Example 1 mentioned above to KETCHIEN carbon, and the acquired carbon support Pt catalyst was made into the comparison catalyst 3.

[0040]About the trial production catalysts 1-19 and the comparison catalysts 1-3 which were acquired, the mean particle diameter of the alloy particles by a transmission electron microscope was measured as physical-properties evaluation. The alloy degree was evaluated from change of the grating constant of Pt by an X-ray diffraction method. These results and preparing methods of a catalyst are shown in the following table 1. In Table 1, the case of O and the independent metal mixture is described for the case where 2 component metals are alloys as x.

[0041]

[Table 1]

触媒番号 (合金種)	金属コロイドの調製方法			合金平均粒径 (透過型電子 顕微鏡法) (単位nm)	合金の 度合い (○:合金 ×:混合物)
	合金 コロイド 番号	還元剤	調製手順 (* イオン交換水に 還元剤添加後に 2種金属塩添加)		
1 (Pt-Ru)	1	クエン酸ナトリウム	*	3~4	○
2 (Pt-Ru)	2	エタノール	*	2~3	○
3 (Pt-Ru)	3	メタノール	*	3~4	○
4 (Pt-Ru)	4	イソプロパノール	*	3~4	○
5 (Pt-Ru)	5	ブタノール	*	3~4	○
6 (Pt-Ru)	6	酢酸	*	2~4	○
7 (Pt-Ru)	7	ギ酸	*	3~4	○
8 (Pt-Ru)	8	アセトン	*	3~5	○
9 (Pt-Ru)	9	メチルエチルケトン	*	3~4	○
10 (Pt-Ru)	10	ギ酸メチル	*	2~4	○
11 (Pt-Au)	11	クエン酸ナトリウム	*	3~4	○
12 (Pt-Pd)	12	クエン酸ナトリウム	*	3~5	○
13 (Pt-Rh)	13	クエン酸ナトリウム	*	2~4	○
14 (Pt-Ir)	14	クエン酸ナトリウム	*	3~4	○
15 (Pt-Co)	15	クエン酸ナトリウム	*	3~4	○
16 (Pt-Fe)	16	クエン酸ナトリウム	*	2~4	○
17 (Pt-Ni)	17	クエン酸ナトリウム	*	3~4	○
18 (Pt-Cu)	18	クエン酸ナトリウム	*	3~5	○
19 (Pt-Sn)	19	クエン酸ナトリウム	*	3~4	○
比較1 (Pt-Ru)	比較 1	無し	高温還元処理	10~15	○
比較2 (Pt-Ru)	比較 2	クエン酸ナトリウム	*	3~4	×
比較3 (Pt)	比較3	クエン酸ナトリウム	1種のみの 金属コロイド	3~4	1種金属

[0042]The trial production catalysts 1-19 prepared by the method of adding the solution of two kinds of metal salt at the period in the solution in which the reducing agent which consists of organic acid was dissolved have a high alloying degree of an active metal, and it turns out that mean particle diameter of an active metal can be made small so that clearly from Table 1.

[0043]On the other hand, although the comparison catalyst 1 prepared with the elevated-temperature reduction approach can make the alloying degree of an active metal high, it turns out that the mean particle diameter of an active metal becomes large compared with the trial production catalysts 1-19. Although the comparison catalyst 2 prepared by the method of adding the solution of organic acid to the mixed water solution of two kinds of metal salt can make mean particle diameter of an active metal small, it turns out that an active metal continues being not an alloy but a mixture.

[0044][Example 3] The polymer electrolyte fuel cell was manufactured using said trial production catalysts 1, 2, 3, 4, and 5 and the comparison catalysts 1, 2, and 3, and power generation performance when CO contains in the fuel gas supplied to an anode pole was evaluated.

[0045](Preparation of a battery cell) The Nafion solution was added as water / ethanol mixed water, and a polyelectrolyte solution for the catalyst 1, and the slurry was prepared by ultrasonic stirring. The obtained slurry was applied to the Teflon sheet, it transferred to both

sides of the solid polymer membrane (at the Du Pont make, a trade name is the Nafion film) of 50 micrometers of thickness, and the anode pole was formed. The amount of Pt(s) in an anode pole was 0.5 mg/cm^2 , the amount of Ru was 0.25 mg/cm^2 , and Nafion liquid was 0.5 mg/cm^2 . [0046]On the other hand, the Nafion solution was added as water / ethanol mixed water, and a polyelectrolyte solution for the comparison catalyst 3, and the slurry was prepared by ultrasonic stirring. The obtained slurry was applied to the Teflon sheet, it transferred to both sides of the solid polymer membrane (at the Du Pont make, a trade name is the Nafion film) of 50 micrometers of thickness, and the cathode pole was formed. The amount of Pt(s) in a cathode pole was 0.5 mg/cm^2 , and Nafion liquid was 0.5 mg/cm^2 . After sticking carbon paper on an anode pole and each cathode pole, these were inserted with one pair of separators, and the electrode cell 1 of 5 cm around was manufactured. [0047]Except using the trial production catalysts 2-5 and the comparison catalysts 1-3 instead of the trial production catalyst 1 as a catalyst included in an anode electrode, as Example 1 mentioned above explained, the electrode cells 2-5 and the reference electrode cells 1-3 were manufactured. The cathode terminal used in each electrode cells 2-5 and the reference electrode cells 1-3 is the same as that of what is used by the electrode cell 1 mentioned above.

[0048](Power generation performance evaluation) About the electrode cells 1-5 and the reference electrode cells 1-3 which were obtained, a power generation examination is done by the test condition explained below, and the result is shown in the following table 2.

[0049]anode side: -- the H_2 60%, CO_2 20%, N_2 20%, CO10ppm, 3ata, and temperature side of 60 **, and the 50% of hydrogen utilization cathode side -- :air (Air), 3ata, the temperature of 60 **, and 50% of an air utilization rate [0050]

[Table 2]

電極セル番号 (アノード金属、 カソード金属)	電圧(V)	電流密度0. 4 (A/cm^2)	電流密度0. 9 (A/cm^2)
1 (Pt・Ru, Pt)		0. 81	0. 55
2 (Pt・Ru, Pt)		0. 80	0. 56
3 (Pt・Ru, Pt)		0. 79	0. 58
4 (Pt・Ru, Pt)		0. 78	0. 54
5 (Pt・Ru, Pt)		0. 79	0. 54
比較1 (Pt・Ru, Pt)		0. 60	0. 2
比較2 (Pt・Ru, Pt)		0. 50	0. 15
比較3 (Pt, Pt)		0. 40	0. 1

[0051]It turns out that the electrode cells 1-5 using the trial production catalysts 1-5 can obtain high tension compared with the reference electrode cells 1-3 so that clearly from Table 2.

[0052]Although the example using the mixed water solution in which two kinds of metal salt like the mixed water solution of chloroplatinic acid and ruthenium chloride was dissolved was explained in the example mentioned above, Do not use a mixed water solution but two kinds of metallic salt solutions are prepared (for example, solution of chloroplatinic acid and solution of

ruthenium chloride), Except adding these solution at the period, as Examples 1 and 2 mentioned above explained, when the trial production catalysts 1-19 were prepared, the same result was obtained as Table 1 mentioned above explained.

[0053]In the example mentioned above, although the example applied to a binary system alloy like a Pt-Ru alloy was explained, when the preparing method concerning this invention was applied to the alloy containing three or more ingredients, it checked that improvement in an alloying degree and the effect of atomization were acquired.

[0054]

[Effect of the Invention]According to the preparing method of the alloy catalyst which starts this invention as explained in full detail above, the alloying degree of an active metal can be made high, and the particle diameter of an active metal can be made small, and the prominent effect of being able to acquire high activity in the amount of low metal is done so. According to the manufacturing method of the polymer electrolyte fuel cell concerning this invention, the prominent effect of it being able to control that poisoning of the alloy catalyst which contains Pt system alloy as an active metal is carried out by CO, and the activity of said catalyst being improved, and being able to improve battery capacity is done so.

[Translation done.]